OLED degradation described by using a time-dependent local relaxation model

Benoît Racine, Christophe Féry, Armand Bettinelli, Henri Doyeux and Salvatore Ciná
Thomson R&D France
1, Avenue Belle Fontaine – CS 17616
35576 Cesson-Sévigné – France

ABSTRACT

The main mechanisms responsible for the luminance degradation in OLEDs driven under constant current has not yet been identified. In this paper we propose a new approach to describe the intrinsic mechanisms involved in the OLED aging. We will first show that a stretched exponential decay can be used to fit almost all the luminance vs time curves obtained under different driving conditions. In this way we are able to prove that they can all be described by employing a single free parameter model.

By using as an approach based on local relaxation events, we will demonstrate that a single mechanism is responsible for the dominant aging process. Furthermore, we will demonstrate that the main relaxation event is the annihilation of one emissive center.

We will then use our model to fit all the experimental data measured under different driving condition, and show that by carefully fitting the accelerated luminance lifetime-curves, we can extrapolate the low-luminance lifetime needed for real display applications, with a high degree of accuracy.

INTRODUCTION

OLED degradation is one of the main issues the industry has to face in order to make this technology sufficiently reliable for mass production. Particularly, differential degradation between the three primary colours, sticky image effects, as well as degradation under harsh storage conditions, need to be more deeply understood. Despite the importance of the issue, a limited number of studies have been published so far [1-4], and, as consequence, the main mechanisms determining the degradation are still not well understood.

One problem still to be solved is also how to fit the luminance-time (L-t) curve in order to estimate the half-life (defined as the time needed for the luminance to reach 50% of its initial value, when driven at constant current) at useful luminance value.

Thanks to improvements achieved in both device structure and materials quality, the lifetimes (LT) at luminance values needed for real display applications are today of the order of hundred-thousand hours. In order to estimate these values in a reasonable amount of time, accelerate testing conditions, both using higher luminance or higher temperature, are normally done. However, accelerations might introduce other aging mechanisms, making the estimation of the LT a complex issue.

The fit of the L-t curves over a limited range of time, also appears to be a critical problem.

A widespread approach is to describe the L-t curve by using a combination of exponential decays, commonly using two terms, the first-one accounting for the rapid initial decay, the second-one for the long-term degradation, as shown in equation 1.

$$\frac{L}{L_0} = ae^{-\alpha t} + be^{-\beta t} \tag{1}$$

where L_0 is the initial luminance, and a, b, α, β, are fitting parameters.
However, this is extremely dependent on how and when the fit is done, as can be shown in figure 1, where fit with equation 1 has been done after approximately 1000 h and 2000 h LT, extrapolating respectively 3600 h and 4400 h half-life.

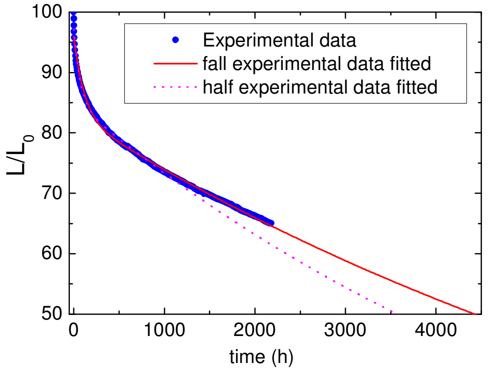

Figure 1. Typical L-t curve at L_0=800 cd/m^2, showing the experimental data (full circles), together with the fit using equation (1) after 1100 h (dotted line), and the 2200 h (full line).

A far better way is to use a stretched exponential decay (SED), as previously reported [5,6], and shown in equation (2). However, a physical justification for using the SED has so far never been found.

$$\frac{L}{L_0} = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{2}$$

In the following sections we will prove that the SED can be successfully used to fit all the L-t curves measured at different initial luminance. We will also show that the coefficient β is constant when changing the initial luminance, reducing the fit to a single parameter (τ). This will strongly improve the predictive nature of the fit, when used to extrapolate lower and more realistic initial luminance curves. More importantly, we will explain the origin of the SED behaviour, when used to describe aging processes with a constant input, as those observed when degrading an OLED at constant current.

EXPERIMENTAL

We used a multi-layer, green-phosphorescent structure, employing an n-doped electron transport layer (ETL) and a p-doped hole transport layer (HTL) respectively for electron and hole injection. The OLED is deposited on glass with the following structure: ITO (150 nm) / HTL (p-doped) 80 nm / EBL 7 nm / EML (green doped) 30 nm / HBL 7 nm / ETL (n-doped) 20 nm / Al 200 nm.

Where EBL is the electron blocking layer, EML is the emissive layer, and HBL is the hole blocking layer.

The samples were fabricated using a standard vacuum deposition process. The ITO substrate were cleaned by a wet process followed by O_2 plasma treatment just before the HTL deposition. The devices were then encapsulated by cover glass and getters, in inert atmosphere.

Each sample contains 6 identical pixels. Four of them have been LT tested, while two pixels have been kept untouched as a reference. Attention has been paid that no black spots had been developed during the OLED aging.

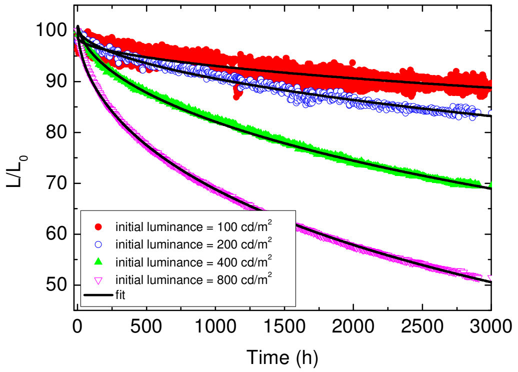

Figure 2. L-t curves measured at various initial luminance values. Black lines are the fits with equation 2, using a constant value for β=0.53 and using τ as the only fit parameter.

Figure 2 shows the experimental L-t data at different initial luminance values, together with the fits using equation 2 at constant β=0.53, determined by fitting the L-t at L_0=800 cd/m^2. We can see that the SED with fixed β can be used to fit all the L-t curves with a high degree of accuracy. The estimated LTs are shown in figure 3, together with the fit using the well known relation:

$$L_0^m \; t_{1/2} = const \qquad (3)$$

where m=1.7 (in this particular case, but dependent on the device structure and the emissive material) is the acceleration coefficient, and $t_{1/2}$ is the half-life. A LT value in excess of 100.000 h is estimated at L_0=100 cd/m^2.

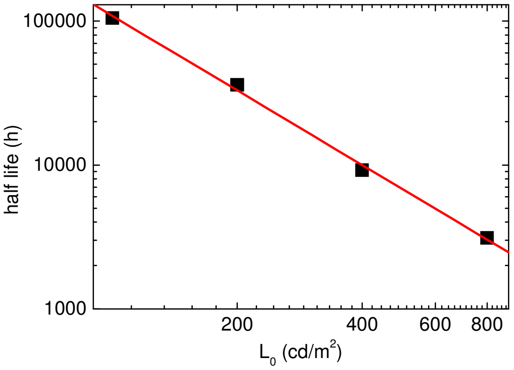

Figure 3. Estimated half-life using the SED with constant *β*=0.53 (full squares), together with the fit using equation 3 (line).

DATA ANALYSIS AND MODELLING

Following the LT test, the samples have been analysed with a fluorescent microscope. We used photo-luminescence (PL) spectroscopy to measure the PL intensity of the various pixels, two stored (L_0=0), and four degraded. The samples were irradiated with blue light at fixed intensity, while the PL signal was collected into a calibrated spectrometer (Spectrascan PR 650). The residual (after LT test or storage) PL intensity was recorded, and is shown in Figure 4, together with the residual electro-luminescence (EL) derived from Figure 2.

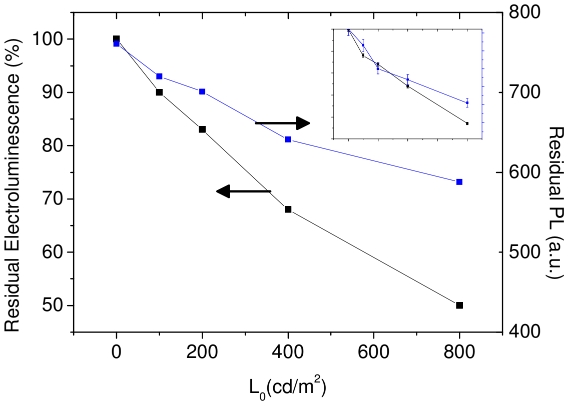

Figure 4. Residual PL and EL measured on both the degraded and stored (L_0=0) pixels. The insert shows similar experimental data measured on a different sample with thinner EML.

We observe that the residual PL follows the same trend as the residual EL, showing that the annihilation of the emissive centers (ECs) is likely to be one of the main reasons for the OLED degradation. The smaller relative decrease in PL compared with the EL (~25% compared with ~ 50%) can be attributed to the reason that both excitons formation and recombination, only takes place on part of the EML.

To confirm this point, we have done the same experiment on a sample having a much thinner EML (~16 nm). The results, shown in the insert of Figure 4, clearly show that the relative change in PL and EL gets closer when the EL gets thinner, i.e. when the light emission takes place on a larger portion of the EML.

From what we have observed, we can conclude that the degradation measured in EL is dominated by the annihilation of the ECs inside the EML.

In order to model the OLED aging, we consider other degradation processes observed in different systems, like degradation of SiO_2 under constant pressure. It has been demonstrated that, in these systems, the aging rate decreases when the total aging increases [7].

We formulate the hypothesis that, the probability to annihilate an isolated EC, is proportional to $exp\text{-}(U_0/kT)$, where U_0 is the energy needed to degrade an isolated EC.

This probability is increased due to the presence of all the other ECs, as shown in equation 4.

$$U(n) = U_0 - \varepsilon(n_s - n) \tag{4}$$

Where n_s and n are respectively the total number of ECs at $t=0$ and the number of degraded EC at a time t and ε is a coupling constant.

We assume that once an EC is degraded, it doesn't play any role within the system, and that the probability of degrading an EC decreases while aging the OLED. This is because the number of EC that could contribute to the degradation of the others ECs, through processes like radiative or non-radiative recombination, decrease while the OLED ages.

Therefore, the rate equation for the number of degraded EC, n, can be written as

$$\frac{dn}{dt} = \frac{1}{\tau_0}\exp\left(-U(n)/kT\right) - Cn \tag{5}$$

Cn is used to accounts for saturation, i.e. $dn/dt = 0$ when $t \to \infty$. The constant $1/\tau_0$ represents the EC relaxation rate.

By combining equation 4 and 5, we obtain the differential equation 6, whose solution gives the number of damaged EC at time t as function of ε and n_s

$$\frac{1}{\tau}\frac{dn}{dt} = \exp\left(-An\right) - \frac{n}{n_S}\exp\left(-An_S\right) \tag{6}$$

Where $A = \varepsilon n_S$ and $\tau = \tau_0 \exp\left(\frac{U_0 - A}{kT}\right)$

We define $L(t)/L_0=(1-n/n_s)$. This quantity should represent the luminance degradation of an OLED, as those shown in Figure 2.

In Figure 5 we find the same experimental data as in Figure 2, while the fits are now done by using $L(t)/L_0$ obtained by numerically solving equation 6, and using n_s=1

It has been demonstrated [7] that the numerical solution of equation 6 family, can be very well fitted by using the SED.

This explains why equation 6 and the SED give very similar results when used on the same experimental data. It also shows, for the first time, the physical meaning behind the use of the SED to fit the luminance degradation of an OLED under constant driving conditions.

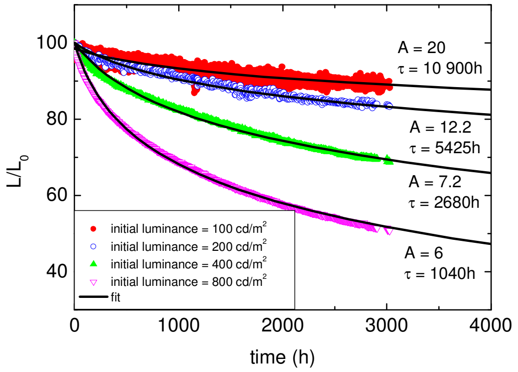

Figure 5. Experimental data as in Figure 2 (full dots). The continuous lines are fits with L/L_0 obtained by numerically solving equation 6.

CONCLUSIONS

We have shown that the SED can be used to accurately fit the OLED LT. We have also found out that the determination of low luminance LT starting from accelerated measurements, can be reduced to a single free parameter problem, greatly improving the accuracy of the half-life prediction.

Furthermore, we have shown for the first time that the annihilation of the ECs is the main mechanism responsible for the OLED degradation. This single mechanism is sufficient to account for both the initial rapid decay, as well as for the long term degradation observed in the L-t curve. We have proposed a model that describes with a high level of accuracy the degradation process, and justifies the use of the SED to fit the LT experimental curves.

ACKNOWLEDGMENTS

We wish to thank Dr W.E. Howard for useful discussions.

REFERENCES

1. I.D. Parker *et al*, J of App. Phys., **85**, 2441, 1999
2. P.E. Burrows *et al*, App. Phys. Lett., **76**, 2493, 2000
3. G.C.M. Silvestre *et al*, App. Phys. Lett., **78**, 1619, 2001
4. H. Aziz and Z.D. Popovic, App. Phys. Lett., **80**, 2180, 2002
5. W. E. Howard and O. F. Prache, IBM J. RES. & DEV., **45**, 1, 2001
6. M. Ishii, R&D Review of Toyota CRDL, **38**, 2
7. K Trachenko and M. T. Dove, Phys. Rev. B, **70**, 132202, 2004